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Material Dependence of Electron Inelastic Mean Free Paths at Low Energies

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We have calculated electron inelastic mean free paths (IMFPs) for 50-2000 eV electrons in 31 materials (27 elements and 4 compounds). We present and discuss in this paper IMFP data for aluminum and gold in the 50-200 eV range. Substantial differences are found in the shapes of the IMFP versus energy curves and these can be understood in terms of the different inelastic scattering mechanisms in the two metals. The minimum IMFP value occurs at 40 eV in aluminum and at 120 eV in gold, a result which is consistent with the trends expected from free-electron IMFP calculations. This result differs, however, from that expected from the Seah and Dench attenuation length formula which shows essentially no material dependence at low energies. We have extended a general formula derived earlier to describe the calculated IMFPs over the 200-2000 eV energy range to give the IMFP dependences on material and energy from 50 to 2000 eV.

I. Introduction

Values of electron inelastic mean free paths (IMFPs) and attenuation lengths (ALs) are needed for quantitative surface analyses by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) as well as for determining the surface sensitivity of other electron spectroscopies. The terms IMFP and AL are often used interchangeably but each has a separate meaning.[1,2] The IMFP can be obtained from theory and certain types of experiments, while the AL is obtained from overlayer-film experiments and with use of a model in which the effects of elastic electron scattering are ignored. Another related term, the escape depth, is the product of the AL and the cosine of the angle defined by the analyzer direction and the surface normal (e.g., in an AES or XPS experiment).[1] The IMFP is systematically larger than the AL by up to about 35%.[3]

We address in this paper the extent to which IMFP and AL values depend on material at low electron energies (< 200 eV). Seah and Dench[4] analyzed AL data available prior to 1979 and found that they could be adequately represented by the equation

$$\lambda_A = A_i E^{-2} + B_i E^{0.5} \qquad (1)$$

where E is the electron energy (in eV) with respect to the Fermi level, and A_i and B_i are parameters different for three groups of materials (elements, inorganic compounds, or organic compounds). For elements, the AL equation is

$$\lambda_A = 538\ E^{-2} + 0.41\ (aE)^{0.5} \text{ monolayers} \qquad (2)$$

where a is the average thickness of a monolayer given by

$$a^3 = 10^{24} M/\rho N \quad \text{nm} \qquad (3)$$

and M is the atomic weight, ρ is the bulk density (in kg m^{-3}), and N is Avogadro's number.

It is well known that plots of AL or IMFP values versus electron energy have a minimum in the vicinity of 50 eV. Simple manipulation of Eq. (2) indicates that the energy for the AL minimum in elements is

$$E_{min,A} = 30.8\ a^{-0.2}\ eV \tag{4a}$$

at which the AL value is

$$\lambda_{min,A} = 2.85a^{0.4}\quad \text{monolayers} \tag{4b}$$

The value of $E_{min,A}$ depends very weakly on a; for values of a between 2 and 3 Å, $E_{min,A}$ is between 39 and 43 eV and $\lambda_{min,A}$ is between 3 and 5.3 Å. Analysis of ultraviolet photoemission data, however, has indicated that $E_{min,A}$ varied between about 10 and 100 eV and $\lambda_{min,A}$ varied between about 1 and 4 Å for different elements.[5]

Early IMFP calculations[6] for jellium, a fictitious material of variable density, showed that the energy for the IMFP minimum, $E_{min,I}$, ranged between 20 and 100 eV while the corresponding IMFP value $\lambda_{min,I}$ was almost constant at about 3.5 Å. These calculations were made for a range of densities that corresponded to those encountered in real solids. The dominant inelastic electron scattering mechanism in jellium, however, is bulk plasmon excitation; bulk plasmon excitation is the most significant scattering mechanism in so-called free-electron solids (e.g., Mg, Al, Si, and Ge) but not for transition and noble metals.[7]

We have previously reported[8] new calculations of IMFPs for 200-2000 eV electrons in 27 elements (C, Mg, Al, Si, Ti, V, Cr, Fe, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Bi) and 4 compounds (LiF,

SiO_2, ZnS, and Al_2O_3). We fitted our calculated IMFPs to the Bethe equation for inelastic electron scattering in matter and were able to obtain empirical expressions for the two Bethe parameters in terms of several material constants. The resulting general formula, to be referred to later as TPP-1, could then be used to predict IMFPs in other materials.

Our IMFP calculations have now been extended to lower energies (50 eV).[9] We present energy dependences of the IMFP for two prototypical metals, aluminum and gold, which are free-electron-like and non-free-electron-like, respectively. We compare these results with those expected from Eqs. (2)-(4) for AL values and from free-electron theory for IMFP values. We also report on a new general IMFP formula for the 50-2000 eV energy range.

2. Procedure

Our IMFP calculations are based on an algorithm developed by Penn[10] which should be applicable to a wide range of materials. Experimental optical data are used to give information on the inelastic scattering probability as a function of energy loss for each material and theory is used to describe the dependence of the scattering probability on momentum transfer. This hybrid approach enables us to take advantage of available optical data which has been checked for internal consistency with two sum rules.[8] We are particularly interested in using the algorithm in a consistent way to determine IMFP dependence on material and electron energy since AL measurements are extremely difficult to perform with the necessary accuracy.[1,11]

The IMFPs are calculated from Eqs. (1) and (14) of our previous paper.[8] The IMFP values reported in that paper were obtained with an approximation valid above 200 eV; this approximation was not used here. The Penn algorithm neglects vertex corrections, self-consistency, and the effects of exchange and

correlation; we believe our results will be useful for electron energies above about 50 eV.[8,12]

IMFP calculations were made for the same 27 elements and 4 compounds we examined previously;[8] these materials were selected because suitable optical data were conveniently available. The methods by which the optical data were checked have been reported.[8] Values of the energy-loss function $\mathrm{Im}[-1/\epsilon(\Delta E)]$ were calculated from the complex dielectric constant $\epsilon(\Delta E)$ as a function of electron energy loss ΔE (or photon energy).

All energies are reported here with reference to the Fermi level. A parameter in the IMFP calculation is the Fermi energy (or width of the conduction band); these values have been taken from band-structure calculations for the elemental solids.[13] It was found that the calculated IMFPs were not sensitive to this parameter and so estimates from free-electron theory were made for the four compounds.

3. Results and Discussion

Figure 1 shows plots of the calculated IMFPs below 200 eV for aluminum and gold. Although the IMFP values at energies below 50 eV may not be reliable, we present these results to show the trends of the IMFP dependence on energy in the vicinity of the IMFP minima in different materials.

The Al plot in Fig. 2 has a steep decrease of the IMFP with increasing energy, a minimum of 3.1 Å near 40 eV, and an increase of the IMFP to higher energies. This curve is similar to that found with other free-electron-like solids.[9] For Mg, Al, and Si, the minimum IMFP values are in the range 3.1-4.1 Å and occur at energies between 30 and 40 eV.[9] The energies for the minima scale with the plasmon energies in these solids, as expected from the IMFP calculations for jellium.[6] The variations we find in the minimum value of the

IMFP for the three elements, however, are not expected from the jellium IMFP calculations.[6] Our IMFP plots for Mg, Al, and Si have minima at energies close to the values expected from the AL formula of Seah and Dench,[4] as indicated by Eq. (4a), and the minimum IMFP values are similar to the AL values expected from Eq. (4b).

The Au plot in Fig. 1 is qualitatively different from that for Al. The IMFP decreases more gradually with increasing energy and has a broad minimum; the minimum IMFP value is 4.7 Å at 120 eV. The IMFP plot for Au is qualitatively similar to those of other non-free-electron-like metals such as Ni and Cu.[9] All three metals show broad minima in the IMFP versus energy plots with minimum IMFP values between 4.5 and 4.8 Å at energies between 70 and 120 eV. The energies at which the minima occur are much higher than those expected from the Seah and Dench AL formula [Eq. 4(a)]. The IMFP calculations for jellium, however, indicate that the IMFP minima should occur for energies greater than 100 eV for electron densities corresponding to Ni, Cu, and Au.[6] Since jellium is not a good model for a transition or noble metal, we believe that the agreement between the positions of the minimum IMFP values and the general trends expected from the jellium calculations is satisfactory.

It is well known that the inelastic electron scattering in transition and noble metals cannot be well described by free-electron theory.[7] There are multiple inelastic scattering channels (i.e., not a single plasmon excitation as in the free-electron-like solids). The electron energy-loss spectra consist of broad, overlapping structures in the 10-80 eV energy-loss range and these overlap with the structures due to core-electron excitations to an extent that makes it impossible to make meaningful distinctions between them.[7] The broad minimum for Au in Fig. 1 is consistent with the broad energy-loss spectrum for

this metal.

We have previously analyzed our calculated IMFPs for energies between 200 and 2000 eV with the Bethe equation[14] for inelastic electron scattering.[8] This equation has been modified[9] in order to fit our IMFP data for 31 materials over the 50-2000 eV range by the addition of two terms (as proposed by Inokuti[15] and Ashley[16]):

$$\lambda = E/(E_p^2\,[\beta \ell n(\gamma E) - C/E + D/E^2]) \quad \text{Å} \tag{5}$$

where $E_p = 28.8\ (N_v \rho/M)^{1/2}$ is the free-electron plasmon energy (in eV), ρ is the bulk density (in g/cm^3), N_v is the number of valence electrons per atom or molecule, and β, γ, C, and D are parameters that can be expressed as:

$$\beta = -0.0216 + 0.944/(E_p^2 + E_g^2)^{1/2} + 7.39\times10^{-4}\rho \tag{6}$$

$$\gamma = 0.191\ \rho^{-0.50} \tag{7}$$

$$C = 0.0650/U^2 - 0.130/U + 1.11 \tag{8}$$

$$D = 1.91/U^2 - 5.12/U + 35.3 \tag{9}$$

The term E_g is the bandgap energy (in eV) for nonconductors and $U = N_v \rho/M$. Equations (6) and (7) are similar to the corresponding equations derived earlier in fits to the IMFP data over the 200-2000 eV range to give TPP-1, a general formula to predict IMFPs for this energy range.

Equations (5)-(9) constitute a new general formula for IMFPs over the 50-2000 eV range and will be referred to as TPP-2. As examples, Figs. 2 and 3 show plots of our calculated IMFPs for energies below 200 eV for Aℓ and Au, fits to these data with Eq. (5), and IMFP values predicted by TPP-2 (using appropriate values of the parameters for each material). It can be seen that TPP-2 provides a reasonable representation of the calculated IMFPs, particularly the very different IMFP-energy dependences in Aℓ and Au. We

believe that TPP-2 can be used as an approximate guide to the material and energy dependences of AL values.

4. Summary

We have calculated electron IMFPs over the 50-2000 eV energy range in 31 materials. IMFP data for aluminum and gold in the 50-200 eV range are presented here as examples of the substantial differences we have found in the shapes of the IMFP versus energy plots at low energies. The minimum IMFP value is found at about 40 eV for Aℓ while that for Au occurs at 120 eV. These differences can be understood in terms of the different inelastic scattering mechanisms in the two metals.

The differences in the shapes of the IMFP-energy curves at low energies also indicate a limitation of the AL formula of Seah and Dench[4] which yields an essentially material-independent AL minimum at an energy of about 40 eV. Our results do agree with the trends expected from IMFP calculations in jellium of different density.[6]

We have found that our IMFP values could be fitted by a modified form of the Bethe equation and that the four parameters in this equation could be empirically related to several material constants. The resulting general formula represents adequately the different IMFP versus energy plots for our 31 materials and can be used to predict IMFP values in other materials (over the same range of electron energies).

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Figure Captions

Fig. 1. Plots of the calculated IMFPs for aluminum (solid line) and gold (dashed line) as a function of electron energy.

Fig. 2. Comparison of calculated IMFP values for aluminum (open circles) with the fit (solid line) using the modified Bethe equation [Eq. (5)], and the predictions (dashed line) of the general formula TPP-2 [Eqs. (5)-(9)] using values of parameters for Aℓ.

Fig. 3. Comparison of calculated IMFP values for gold (open circles) with the fit (solid line) using the modified Bethe equation [Eq. (5)], and the predictions (dashed line) of the general formula TPP-2 [Eqs. (5)-(9)] using values of parameters for Au.

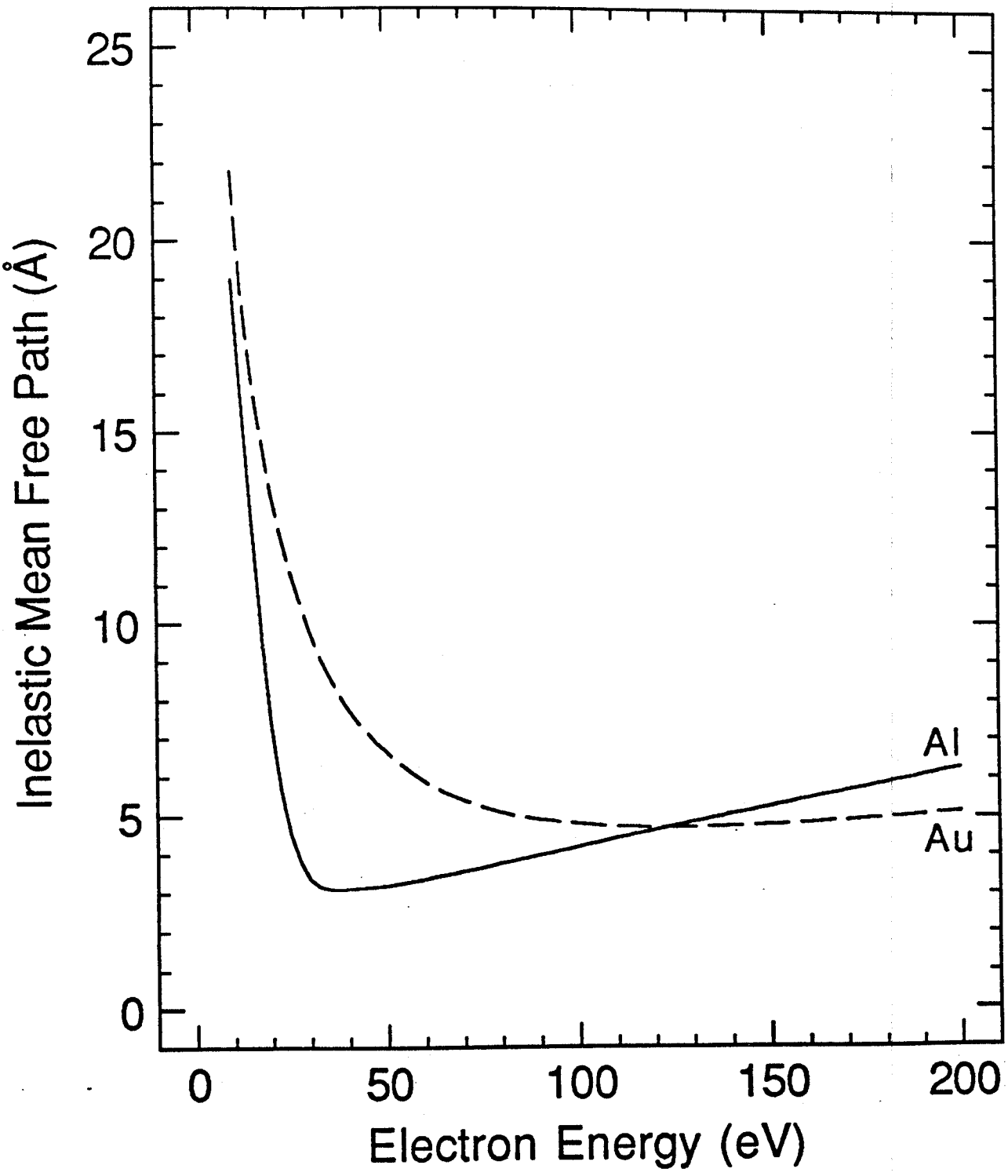
Inelastic Mean Free Path (Å)
25
20
15
10
5
0
0
50
100
150
200
Electron Energy (eV)
Al
Au

Fig. 1.

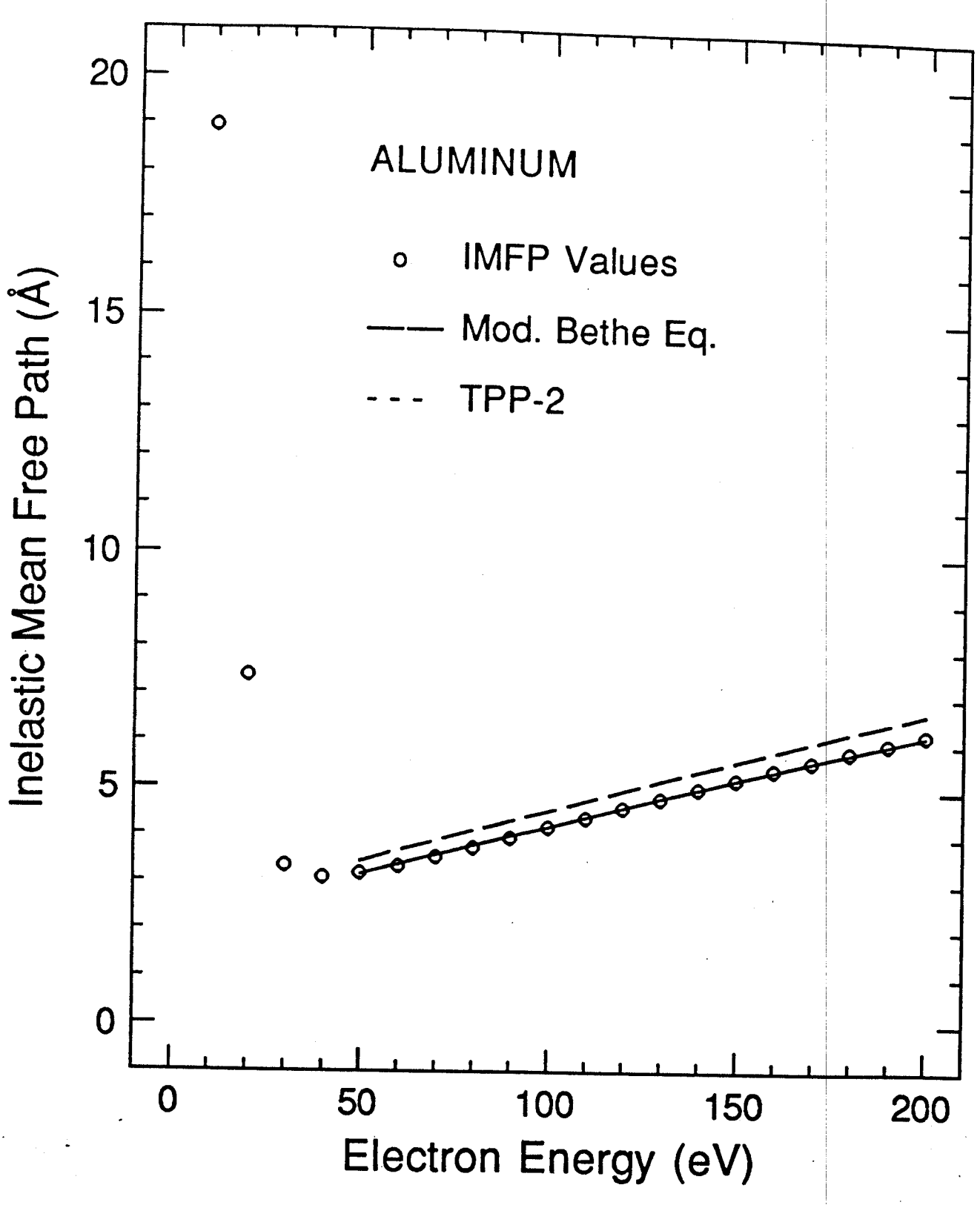
ALUMINUM
IMFP Values
Mod. Bethe Eq.
TPP-2
Inelastic Mean Free Path (Å)
Electron Energy (eV)
0
5
10
15
20
0
50
100
150
200

Fig. 2.

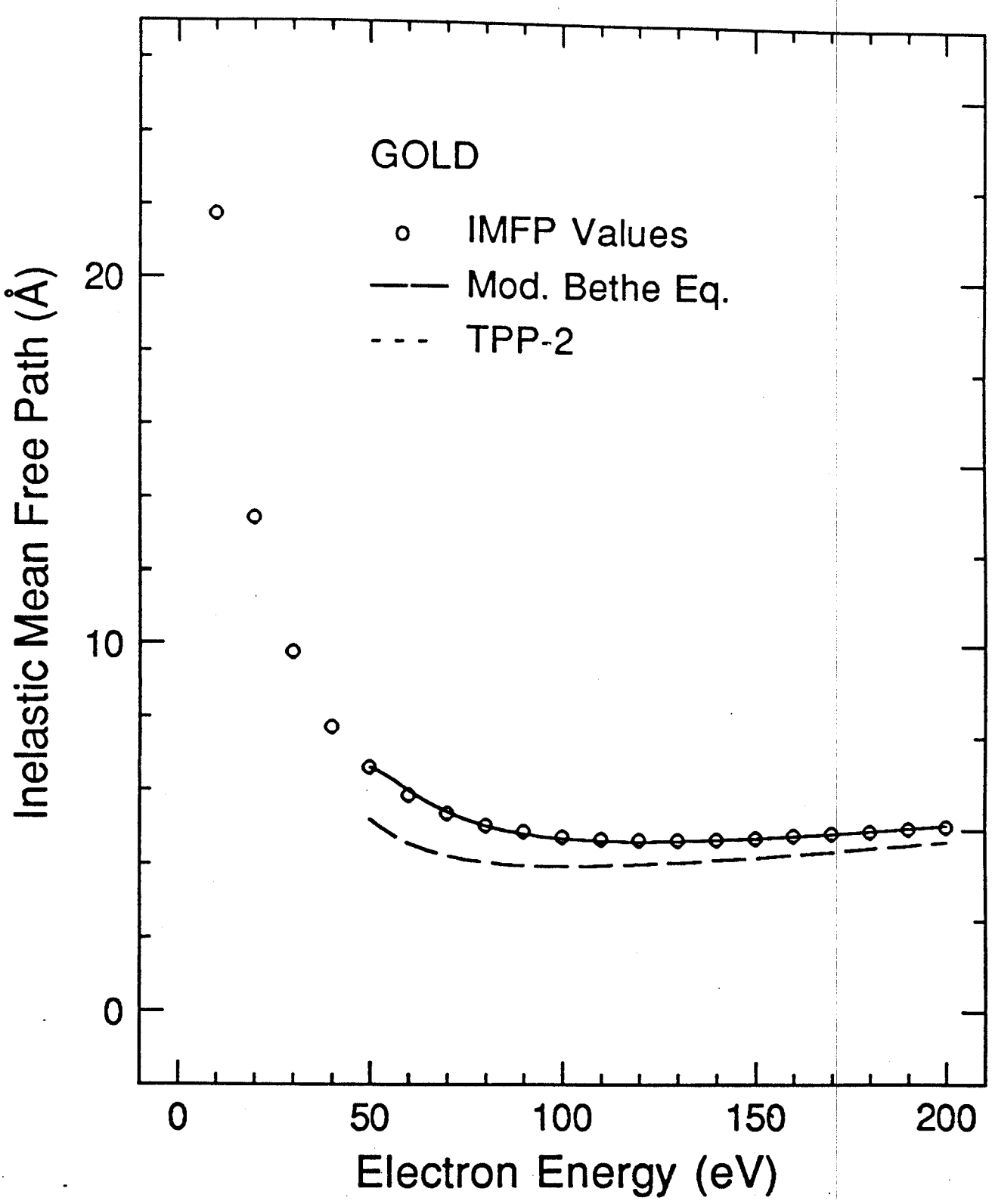
GOLD
IMFP Values
Mod. Bethe Eq.
TPP-2
Inelastic Mean Free Path (Å)
20
10
0
0
50
100
150
200
Electron Energy (eV)

Fig. 3.